PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : H05K 3/06

A1

(11) International Publication Number: WO 97/15173

(43) International Publication Date: 24 April 1997 (24.04.97)

(21) International Application Number: PCT/US96/15944

(22) International Filing Date: 4 October 1996 (04.10.96)

(30) Priority Data:
08/543,943 17 October 1995 (17.10.95) US

(71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventors: ISBERG, Thomas, A.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). WOLK, Martin, B.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). DOWER, William, V.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). ZENNER, Robert, L., D.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). CHOU, Hsin-Hsin; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: GWIN, H., Sanders et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: METHOD FOR RADIATION-INDUCED THERMAL TRANSFER OF RESIST FOR FLEXIBLE PRINTED CIRCUITRY

(57) Abstract

A dry, high-resolution process for preparing printed circuits comprising the laser induced thermal transfer of a resist material is described. A donor element is prepared by coating a substrate with a resist material comprising a light-to-heat converter and an optional adhesive layer. The donor element is placed in intimate contact with a metal-coated surface of a receiving element. The donor element is imagewise irradiated (e.g., with a laser or flash lamp) with electromagnetic radiation under conditions sufficient to thermally transfer the resist material from the donor element to the metal-coated surface of the receiving element. In one embodiment, the resist-coated receiving element is then etched to give the printed circuit directly. Alternatively, the resist-coated receiving element may be plated-up, the resist removed, and the thin metal surface remaining where the resist was present may be etched away to give a printed circuit.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

METHOD FOR RADIATION-INDUCED THERMAL TRANSFER OF RESIST FOR FLEXIBLE PRINTED CIRCUITRY

Field of the Invention

This invention relates to the production of patterned resists on metal-coated flexible substrates. The pattern can be produced directly on a metal-coated surface of a receiving element by radiation-induced thermal transfer of a resist material from a donor element to the receiving element.

Background

Various printing techniques (e.g., screen printing, electrophotographic printing, etc.) known in the art have been used to apply resists to metal foils for use in the preparation of printed circuit boards. For example, see U.S. Pat. Nos. 2,441,960 and 2,947,625. However, the resolution of the printed circuits made by these techniques is limited by the available resolution of the printing technique.

The manufacture of high resolution printed circuits has generally required the use of photolithographic processes. Preparation of artwork is required to prepare the photoresists to be used in the photolithographic process. A digital pattern to represent the desired printed circuit is created in a file using commercially available software (e.g., CAD). The digital information in the file is then transferred to a scanner which generates a film. The film is then developed, processed, and saved to be used later to expose the photoresist.

A photoresist material is either laminated or coated (e.g., spin coated) on a metal-coated surface. If the photoresist material is coated from a solvent, it is then dried. Until it has been exposed and developed, the photoresist material must be protected from the wavelength of light for which it has been sensitized. The photoresist material is then exposed through the above-created film for the proper length of time with either a visible or UV light source as required, the length of exposure depending on the type and intensity of the light source, the thickness and type of photoresist material being used, the D_{min} and D_{max} of the film, and the type of pattern being created. After exposure, the photoresist-coated metal is wet-processed to remove the photoresist material image-wise. The printed circuit is then created by either etching the exposed metal and removing the photoresist or,

alternatively, plating-up the exposed metal areas, removing the photoresist, and etching away the thin metal in areas where the photoresist was present after pattern-wise removal.

While the above process has been shown to be commercially successful in large scale manufacturing operations, there is a need in the industry for simplified processes to prepare printed circuits requiring fewer steps resulting in shorter cycle times. Such simplified processes are especially attractive when short run, specialized, or prototyped printed circuits are required.

One alternative process has been reported in which a thermal printer is used to apply a conductive ink to a circuit board substrate (Research Disclosure 31161, March 1990). A thermal printhead is used to transfer the conductive ink from a specially formulated ribbon to the substrate. The ink is cured using either heat or radiation, and the circuit board is then plated. The system reportedly offered advantages over known systems including easily generated patterns and high resolution.

Another method of producing printed circuits has been reported in which a preformed resist pattern is thermally transferred to a metal foil (Jap. Pat. No. 59-031870). A resist pattern of toner on paper is created using a plain paper copier. The resist pattern is pressed against the surface of copper foil and heated. The melted toner adheres to the foil, and the paper is removed, resulting in the transfer of the resist pattern to the metal surface. Etching the exposed metal results in the printed circuit.

Several methods have been disclosed to pattern a resist covering a metal foil which use light to ablate or remove the resist material in the exposed areas. U.S. Pat. No. 3,547,629 discloses a method for photopatterning a resist by photoflashing a light through a mask onto a substrate coated with a photoflash pyrolyzable layer (e.g., copper foil coated with a nitrocellulose lacquer). U.S. Pat. No. 4,414,059 discloses a far UV process for patterning resist materials involving ablative photodecomposition of the resist material. U.S. Pat. Nos. 4,780,177; 4,842,677; and 5,364,493 disclose the use of lasers to photopattern a resist material.

Laser-induced thermal transfer of materials from a donor sheet to a receptor layer has been described in the patent and technical literature for nearly thirty years. However, few commercial systems have utilized this technology. Exposure fluences required to transfer materials to a receptor have been, at best, on the order of 0.1 Joule/cm^2 (i.e., J/cm^2). Consequently, lasers capable of emitting more than 5 Watts of power, typically water-cooled Nd:YAG lasers, have been required to produce large format images (A3 or larger) in reasonable times. These lasers are expensive and impractical for many applications. More recently, single-mode laser diodes and diode-pumped lasers producing 0.1-4 Watts in the near-infrared region of the electromagnetic spectrum have become commercially available. Diode-pumped Nd:YAG lasers are good examples of this type of source. They are compact, efficient, and relatively inexpensive.

Separately addressed laser diode arrays have been utilized to transfer dyes in color proofing systems. For example, U.S. Pat. No. 5,017,547 describes the binderless transfer of dye from a dye-binder donor sheet to a polymeric receptor sheet. In that process, dye molecules are vaporized or sublimed via laser heating. These molecules traverse the gap between the donor and receptor and recondense on the receiver. The donor and receptor are separated by spacer beads.

U.S. Pat. Nos. 5,171,650 and 5,256,506 disclose methods and materials for thermal imaging using an "ablation-transfer" technique. The donor element for that imaging process comprises a support, an intermediate dynamic release layer, and an ablative carrier topcoat. The topcoat carries the colorant. The dynamic release layer may also contain infrared-absorbing (light-to-heat conversion) dyes or pigments. One suggested use for the above process is the preparation of exposure masks (i.e., photomasks) for use in graphic arts or the production of printed circuits.

Published PCT Application WO 93/03928 discloses peel apart elements for laser-induced thermal imaging. One disclosed element comprises a cover sheet; an adhesive layer; an active layer comprising an infra-red absorbing material and a binder; a support; a photopolymerizable layer; and a substrate. After imagewise laser exposure, the cover sheet and adhesive layer are peeled apart, with the active

layer remaining attached to the support in the exposed areas. The active layer serves as an integral photomask for the photopolymerizable layer. A suggested use for this process is in the preproduction of printed circuit boards.

U.S. Pat. No. 5,278,023 discloses laser-addressable thermal transfer materials for producing color proofs, printing plates, films, printed circuit boards, and other media. The propellant contains a substrate coated thereon with a propellant layer wherein the propellant layer contains a material capable of producing nitrogen (N_2) gas; a radiation-absorber; and a thermal mass transfer material. The thermal mass transfer material may be incorporated into the propellant layer or in an additional layer coated onto the propellant layer. The radiation-absorber may be employed in one of the above-disclosed layers or in a separate layer in order to achieve localized heating with an electromagnetic energy source, such as a laser. Upon laser-induced heating, the transfer material is propelled to the receptor by the rapid expansion of gas. The thermal mass transfer material may contain, for example, pigments, toner particles, resins, metal particles, monomers, polymers, dyes, or combinations thereof.

U.S. Pat. No. 5,338,645 discloses the use of an infrared laser to selectively vaporize the metal on a three dimensional surface to give the desired circuit pattern.

So far as it is known, before the present invention there was no disclosure of imagewise transfer of a resist material from a donor element to a metal-coated receiving element, followed by either etching or metal plating/etching processes to produce a printed circuit.

Summary of the Invention

The present invention provides methods of preparation for printed circuits involving the imagewise radiation-induced transfer of a resist material from a donor element to a metal-coated receiving element.

In one embodiment, the present invention provides a method for preparing printed circuits comprising the steps of: (a) imagewise exposing a donor element comprising a substrate having coated thereon a resist material comprising a light-to-heat converter dispersed in a binder to electromagnetic radiation under

conditions sufficient to transfer the resist material from the donor element to a metal-coated surface of a receiving element; (b) etching the exposed metal surface of the receiving element; and (c) removing the resist material from the receiving element. Optionally, the resist material contains an adhesive topcoat in step (a).

In another embodiment, the present invention provides a method for preparing printed circuits comprising the steps of: (a) imagewise exposing a donor element comprising a substrate having coated thereon a resist material comprising a light-to-heat converter dispersed in a binder to electromagnetic radiation under conditions sufficient to transfer the resist material from the donor element to a thin metal-coated surface of a receiving element; (b) metal plating the exposed metal surface of the receiving element; (c) removing the resist material from the receiving element; and (d) etching away the areas of the thin metal-coated surface where the resist was present before removal from the receiving element. Optionally, the resist material contains an adhesive topcoat in step (a).

In a preferred embodiment, the source of electromagnetic energy used to induce the transfer of the resist material to a metal-coated surface of a receiving element is either a laser or a flash lamp. When organic polymers are used as binder in the resist material, it is preferred that the organic polymer be a gas-producing polymer and that a flash lamp is used as the source of electromagnetic radiation. With many organic polymers, it is also preferred to use an adhesive topcoat layer as a part of the resist material.

The present invention offers advantages over conventional photolithographic techniques in that circuitry can be created directly from circuitization software without the multistep coating, exposure, and wash steps which are required for current techniques. The inventive process by which the patterned resist can be produced is via radiation-induced thermal imaging. Radiation-induced thermal transfer of the resist material from a donor sheet to a metal-coated receptor surface is a one step, dry, high resolution process. The transfer can be induced by flash lamp exposure or laser exposure during which the light-to-heat converter absorbs the incident radiation and heats the surrounding medium until ablation occurs. In a preferred embodiment, a digital process is used

to control a laser used to induce the transfer of the resist material to the metal-coated surface of the receptor. The flexibility of the digitally-controlled laser-induced transfer process allows different circuit designs to be easily accommodated in the same production flow. The resolution of the method is limited only by the spot size of the laser and the thickness and integrity of the transferred resist. In addition, the process is compatible with web processing techniques for mass production of printed circuits.

As used herein:

"thermally-available nitrogen content" refers to the nitrogen content (weight percentage basis) of a material which upon exposure to heat (preferably less than about 300°C, more preferably less than about 250°C) generates or liberates nitrogen (N_2) gas;

"thermally-decomposable nitrogen-containing group" refers to a nitrogen-containing group (e.g., azido, nitrate, nitro, triazole, etc.) which upon exposure to heat (preferably less than about 300°C, more preferably less than about 250°C) generates or liberates N_2 gas;

"flash lamp" means a device that can convert stored electrical energy into light by means of a sudden electrical discharge;

"light-to-heat converter" means a substance which absorbs incident electromagnetic radiation and efficiently transforms it to thermal energy;

"black body absorber" means any material that has significant absorptions in the UV, visible, and near infrared regions of the spectrum;

"latex adhesive" means a stable colloidal dispersion of polymeric adhesive in an aqueous medium;

"thin metal-coated surface" means a metal-coated surface having a thickness of from about 500-5000 Angstroms;

"group" refers to not only pure hydrocarbon chains or structures such as methyl, ethyl, cyclohexyl, and the like, but also to chains or structures bearing conventional substituents in the art such as hydroxy, alkoxy, phenyl, halo (F, Cl, Br, I), cyano, nitro, amino, etc.; and

"radical" refers to the inclusion of only pure hydrocarbon chains such as methyl, ethyl, propyl, cyclohexyl, isooctyl, *tert*-butyl, and the like.

Other aspects, advantages, and benefits of the present invention are apparent from the detailed description, the examples, and the claims.

Detailed Description of the Invention

The donor element is composed of a suitable substrate coated with a layer of resist material containing: a light-to-heat converter (such as carbon black) dispersed in a binder. An optional adhesive layer can be on top of the resist layer. The carbon black or other material functions as a light-to-heat converter upon exposure to incident electromagnetic radiation and causes a rapid local heating of the binder. Volatilization of binder components leads to the transfer of resist material to the metal-coated surface of the receiving element. The donor element may be provided in any convenient form such as sheets or rolls.

The substrate of the donor element may be any substance upon which the resist material may be coated to prepare the donor element. Preferably, the substrate is transparent (at least transmissive) to the wavelength of light used to induce the transfer of the resist material to a metal-coated surface of a receiving element. Possible substrates include glass, polymeric film, and the like. Possible polymeric substrates include polyester base (e.g., polyethylene terephthalate, polyethylene naphthalate), polycarbonate resins, polyolefin resins, polyvinyl resins (e.g., polyethylene, polypropylene, polyvinyl chloride, polyvinylidene chloride, polyvinyl acetals, and copolymers thereof), hydrolyzed and unhydrolyzed cellulose ester bases (e.g., cellulose triacetate, cellulose acetate), and other conventional polymeric films used as supports in various imaging arts. A transparent polymeric film base of 0.5 to 100 mils is preferred (0.001 to 0.254 cm). Typical examples are those derived from polymers containing repeating, interpolymerized units derived from 9,9-bis-(4-hydroxyphenyl)-fluorene and isophthalic acid, terephthalic acid or mixtures thereof, the polymer being sufficiently low in oligomer (i.e., chemical species having molecular weights of about 8000 or less) content to allow formation of a uniform film. This polymer has been disclosed as one component in a thermal transfer receiving element in U.S. Pat. No. 5,318,938. In the laser-

induced process, the donor substrate is preferably transparent polyethylene terephthalate (PET). In the flash lamp-induced process, the donor substrate is preferably a UV transparent material such as polypropylene.

Preferred binders used in the resist material in the present invention are organic-based binders.

The particular binders chosen will depend upon the type of application the end-user desires. Thermoplastic or thermosetting resins may be used as appropriate. Non-limiting examples of thermoplastic polymers are poly(methyl methacrylate), nitrocellulose, ethylene-vinyl acetate copolymer, polyethylene, ethylene-propylene copolymer, ethylene-acrylate copolymer, acrylic rubber, polyisobutylene, atactic polypropylene, poly(vinyl butyral), styrene-butadiene, polybutadiene, ethylcellulose, polyamides, polyurethanes, and polychloroprene. Non-limiting examples of thermosetting resins are epoxy resins, phenoxy resins, cyanate ester resins, acrylic resins, and the like.

In the laser-induced process, when an organic binder is utilized, it is preferably one that exhibits suitable physical properties for transfer of thin films. For example, it is preferred that the imaged area readily releases from the surrounding unimaged area and transfers completely to the metal-coated receptor surface.

When an organic polymer is used as a binder in flash lamp-induced transfer, gas-producing polymers are preferred. The heating of the binder during the flash lamp exposure causes a partial or total decomposition of the gas-producing polymer. The resultant gas serves to propel the resist from the donor element to the metal-coated layer of the receiving element. Generally, the gas-producing polymer should have a thermally-available nitrogen content greater than about 10 weight percent; preferably greater than about 20 weight percent; and more preferably greater than about 30 weight percent.

The gas-producing polymer may be any polymer that liberates nitrogen gas (N_2) when heated rapidly, such as, for example, by exposure to an infrared laser beam. Polymers that liberate nitrogen gas on heating generally have thermally-decomposable functional groups. Non-limiting examples of suitable thermally-

decomposable functional groups include azido, alkylazo, diazo, diazonium, diazirino, nitro, nitrato, triazole, etc. The thermally-decomposable groups may be incorporated into the gas-producing polymer either prior to polymerization or by modification of an existing polymer, such as, for example, by diazotization of an aromatic amine (e.g., with nitrous acid) or diazo transfer with tosyl azide onto an amine or β-diketone in the presence of triethylamine.

In one preferred embodiment, the azide-containing polymer used as one of the reactants has the following formula:

$$\left(X - (R)_n - \right)_m L \qquad (I)$$

wherein:

X represents a hydroxyl, azide, mercapto, or amino (including mono-alkyl and aryl-substituted amino) group and preferably, X is an azide or a hydroxyl group;

R represents a divalent monomer group, containing a N_3 group, derived from a cyclic ether such as, for example, $-CH_2CH(CH_2N_3)O-$, $-CH_2C(CH_3)(CH_2N_3)CH_2O-$, $-CH(CH_2N_3)CH_2O-$, $-CH_2C(CH_2N_3)_2CH_2O-$, $-CH(CH_2N_3)CH(CH_2N_3)O-$, and $-CH_2CH(N_3)CH_2O-$; a cyclic sulfide such as, for example, $-CH_2CH(CH_2N_3)S-$, $-CH_2C(CH_2N_3)_2CH_2S-$, $-CH(CH_2N_3)CH(CH_2N_3)S-$, and $-CH_2CH(N_3)CH_2S-$; and a cyclic amine such as, for example, $-CH_2CH(CH_2N_3)N\mathbf{R}^1-$, $-CH(CH_2N_3)CH_2N\mathbf{R}^1-$, $-CH_2C(CH_2N_3)_2CH_2N\mathbf{R}^1-$, $-CH(CH_2N_3)CH(CH_2N_3)N\mathbf{R}^1-$, and $-CH_2CH(N_3)CH_2N\mathbf{R}^1-$;

$\mathbf{R}^1$ represents a hydrocarbyl group (e.g., alkyl, aryl, aralkyl, alkaryl, etc.);

L represents a mono-, di-, tri- or tetra-valent alkyl radical. Non-limiting examples of monovalent radicals are methyl and ethyl. Non-limiting examples of polyvalent alkyl radicals are ethylene, methylene, propylene, 1,2,3-propanetriyl, 2-ethyl-2-methylene-1,3-propanediyl, 2,2-dimethylene-1,3-propanediyl, etc. Preferably, **L** is 2-ethyl-2-methylene-1,3-propanediyl;

corresponding to **L**, **m** represents 1, 2, 3, or 4; and

n represents any positive integer greater than 1, preferably greater than 5, more preferably greater than 10.

The foregoing azide-containing polymer of Formula (I) can be made by procedures well known to those skilled in the art of synthetic organic chemistry such as disclosed, for example, in U.S. Pat. Nos. 3,645,917 and 4,879,419.

One or more crosslinking agents may be employed in combination with the azide-containing polymer of Formula (I) to provide coatings having improved strength. The choice of an appropriate crosslinking agent depends on the functional groups on the azide-containing polymer. Thus, if hydroxyl groups are present on the azide-containing polymer, then crosslinking agents for polyols could be employed (e.g., isocyanates). In cases where free-radically polymerizable groups, such as acrylates, are attached to the polymer backbone, a free-radical initiator may be used as a crosslinking agent.

Preferably, a crosslinking agent for polyols is employed in combination with an azide-containing polymer having multiple hydroxyl end groups. Preferred crosslinking agents in this case are polyisocyanates, including but not limited to, hexamethylene diisocyanate; diphenylmethane diisocyanate; bis(4-isocyanatocyclohexyl)methane, 2,4-toluene diisocyanate, etc.

In another preferred embodiment, the azide-containing polymer used as one of the reactants has recurring units of the following formula:

$$-CH_2-\overset{\displaystyle R^2}{\underset{\displaystyle R^3}{\overset{|}{\underset{|}{C}}}}-CH_2-O- \qquad \text{(II)}$$

wherein: R^2 or R^3 each independently represent an N_3-containing group. An example of a preferred azide group is $-CH_2N_3$.

The azide-containing polymer of Formula (II) can be made by procedures well known to those skilled in the art of synthetic organic chemistry such as disclosed, for example, in U.S. Pat. No. 3,694,383.

In another preferred embodiment, energetic copolymers are utilized as reactants having repeating units derived from different monomers, one or more of

which have N_3 groups. Preferably, the monomers are cyclic oxides having three to six ring atoms. Copolymerization of the monomers is preferably carried out by cationic polymerization. The foregoing copolymers and their method of preparation are disclosed in U.S. Pat. No. 4,483,978.

The light-to-heat converter serves to convert incident electromagnetic radiation into thermal energy. For this reason it is generally desirable that the radiation absorber have low fluorescence and phosphorescence quantum efficiencies and undergo little or no net photochemical change upon exposure to electromagnetic radiation. It is also generally desirable for the radiation absorber to be highly absorptive of the incident radiation so that a minimum amount can be used in coatings. Non-limiting examples of radiation absorbers include pigments such as carbon black (i.e., acetylene black, channel black, furnace black, gas black, and thermal black), bone black, iron oxide (including black iron oxide), copper/chrome complex black azo pigments (e.g., pyrazolone yellow, dianisidine red, and nickel azo yellow), black aluminum, and phthalocyanine pigments. In addition to pigments, the radiation absorber may be a dye as described, for example, in M. Matsuoka *Absorption Spectra of Dyes for Diode Lasers*: Bunshin Publishing Co.; Tokyo, 1990.

Preferably, the radiation absorber employed in the donor element absorbs in the near-infrared or infrared region of the electromagnetic spectrum. In some instances, it may be desirable to employ absorbers which absorb in the visible region of the electromagnetic spectrum.

Other material that may be included in the resist material of the present invention include dyes such as those listed in Venkataraman, *The Chemistry of Synthetic Dyes*; Academic Press, 1970: Vols. 1-4 and *The Colour Index Society of Dyers and Colourists*, Yorkshire, England, Vols. 1-8 including cyanine dyes (including streptocyanine, merocyanine, and carbocyanine dyes), squarylium dyes, oxonol dyes, anthraquinone dyes, and holopolar dyes, polycyclic aromatic hydrocarbons, etc.

The donor elements may be prepared by introducing the components for making the resist material layer into suitable solvents (e.g., tetrahydrofuran (THF),

methyl ethyl ketone (MEK), water, toluene, methanol, ethanol, n-propanol, isopropanol, acetone, etc., and mixtures thereof); mixing the resulting solutions at, for example, room temperature; coating the resulting mixture onto the substrate; and drying the resultant coating, preferably at moderately elevated temperatures. The resist material may be coated on the donor element by a variety of techniques known in the art including, but not limited to, coating from a solution or dispersion in an organic or aqueous solvent (e.g., bar coating, knife coating, slot coating, slide coating, roll coating, curtain coating, spin coating, extrusion die coating, etc.), vapor coating, sputtering, gravure coating, etc., as dictated by the requirements of the resist material itself.

The adhesive layer is an optional topcoat which serves to provide enhanced adhesion to the substrate. Any conventional adhesive formulation can be used including, but not limited to, silicones, acrylates, ethylene/vinyl chloride blends, etc.

When organic polymers are used as binders, it has been found that a topcoat of an adhesive such as those sold under the trade designation Daratak 90L from W.R. Grace & Co., Owensburo, KY (an aqueous dispersion of vinyl acetate-dioctyl maleate-2-ethylhexyl acrylate polymer, available from Hampshire Chemical Co., Lexington, MA, 55 wt% solids) often dramatically increases the uniformity of resist transfer as well as improving the adhesion of the resist layer to the metal-coated surface of the receptor during the process steps which follow (e.g., etching, plating-up). The adhesive topcoat may be applied by conventional coating methods including, but not limited to, curtain coating, knife coating, slot coating, extrusion coating, wire-wrapped bar coating, etc.

The receiving element comprises a metal surface, usually a thin metal surface on a support to give the element adequate strength for processing and handling. Commonly used receiving elements comprise a metal-coated surface on a non-conductive support. The receiving element may comprise any convenient form such as a sheet, film, or flexible carrier web.

The support of the receiving element may be any conventional support known to those skilled in the art. Non-limiting examples include polymeric

materials (e.g., PET, polyethylene naphthalate, polyimide, etc.); glass; epoxy materials; ceramic materials; composite materials for printed circuit boards; and paper. It is also possible to laminate copper foil to the receiving element by using a suitable adhesive.

Metal-coating or metal-plating can be accomplished by any method known to those skilled in the art such as sputtering, magnetron ion plating, ion enhanced plating, chemical vapor deposition, and electroless plating. Non-limiting examples of metals which can be coated or plated include copper, nickel, tin, aluminum, silver, gold, or alloys thereof.

The thermal transfer donor element of the present invention is used by placing it in intimate contact (e.g., vacuum hold-down) with a receptor sheet and imagewise heating the thermal transfer donor element. The radiation absorber utilized in the donor element of the present invention acts as a light-to-heat converter. A variety of light-emitting sources can be utilized to provide the radiation source including lasers and flash lamps.

A variety of lasers such as excimer lasers, gas lasers (e.g., argon-ion, krypton-ion, etc.), diode lasers, and solid state lasers (e.g., Nd:YAG, Nd:YLF, Nd:Glass, etc.) may be used as a source of the electromagnetic radiation to induce transfer of the resist material to the metal surface of the receptor. Preferred lasers typically have output powers greater than 100 mW. Lasers emitting a variety of wavelengths may be used in the present invention, including ultra-violet, visible, and infra-red lasers (i.e., wavelengths from 250-1300 nm). The preferred lasers for use in this invention include continuous-wave high power (> 100 mW) laser diodes, fiber-coupled laser diodes, laser diode arrays, and lamp or diode-pumped solid-state lasers, with the solid-state lasers (e.g. diode or diode-pumped) being most preferred. With continuous-wave lasers, the exposure dwell time should be in the range of 0.1 to 50 microseconds, with 0.1 to 10 microseconds preferred. Alternatively, a pulsed laser (such as a Q-switched Nd:YAG) may be utilized, in which case the dwell time is the same as the pulse width, which is typically on the order of 1-10 nanoseconds. Laser fluences are usually on the order of 0.1-5 J/cm^2.

Flash lamps such as xenon flash lamps provide a momentary intense burst of radiation. A xenon flash lamp produces a broad spectrum of bluish white light in a flash of about 2 to 3 milliseconds in duration as described in U.S. Pat. No. 3,914,775. The flash from a xenon flash lamp will provide an amount of radiant energy which is dependent on the electrical energy input from its power supply. The efficiency of the irradiation means in converting energy input to a xenon lamp to radiant flux density received by the material being irradiated is, among other factors, dependent upon the configuration of the lamp, the spacing of the lamp from the material, and the efficiency and configuration of the reflector used in the lamp.

The source of electromagnetic radiation is used to imagewise irradiate the donor element containing the resist material, thereby inducing the transfer of the resist material to the metal-coated surface of the receptor element in the desired pattern. The imagewise exposure may be carried out in any convenient manner as desired. However, in the case of lasers, the imagewise exposure is generally either made by using masks or by directly digitally addressing the laser. Preferably, the laser is digitally-addressed and is capable of writing an arbitrary pattern of resist material on the metal-coated receptor surface. In this situation, the pattern can easily be designed to match the printed circuit application desired. In the case of flash lamps, the imagewise exposure is generally made either by using masks or by focusing the flash with a microlens array.

Masks may be prepared by conventional methods known in the art such as through the use of a photoresist/etching process. The mask is usually made of a material that reflects the incident radiation, and can be coated or deposited on a flexible or a rigid substrate. Materials commonly used to reflect the incident radiation include chrome and/or chrome oxide.

The use of microlens arrays to prepare the patterned resist is amenable to commercial production of a fixed grid resist pattern. Microlens arrays may be fabricated by the well-known method of compression molding of optical thermoplastics such as polycarbonate and poly(methyl methacrylate), PMMA, as described in U.S. Pat. No. 5,300,263. When a flash lamp is used, the binder used

in the donor element should be one which evolves nitrogen gas upon heating. Examples of such binders are disclosed earlier herein.

Any wet chemical etching technique known to those skilled in the art can be used in the present invention. For example, solutions of nitric acid; hydrogen chloride; sulfuric acid and hydrogen peroxide; ferric chloride; or cupric chloride may be used.

The transferred resist may be removed from the metal-coated substrate by any conventional method known to those skilled in the art.

The following non-limiting examples further illustrate the present invention.

EXAMPLES

Internal Drum System

Imaging was performed using an Nd:YAG laser, operating at 1.06 μm in TEM_{00} mode and focused to a 26 μm spot ($1/e^2$) with 3.5 W of incident radiation at the image plane. The laser scan rate was 64 m/sec. Image data was transferred from a mass-memory system and supplied to an acousto-optic modulator which performs the imagewise modulation of the laser. The image plane consists of a 135° drum which was translated synchronously perpendicular to the laser scan direction.

Microlens Arrays

Two different microlens arrays were used. The stamper for the compression molding is a replica of the original tooling, which is fabricated according to the method of U.S. Pat. No. 5,300,263.

Microlens A is an array of spherical lenses, each with a rectangular cross-section 0.33 x 0.11 mm, and was compression molded in 0.007 in. thick polycarbonate at 170°C and 500 psi (3.4×10^6 N/m^2) for 5 minutes. Microlens B is an array of spherical lenses, each of square 0.356 mm cross-section, and was compression molded in 0.007 in. (0.018 cm) thick polycarbonate at 180°C and 300 psi (2.1×10^6 N/m^2) for 3 minutes. Both Microlens A and B have focal lengths in air of approximately 1 mm.

Copper Plated Substrates

Copper sputtered (2000 Å thick) polyimide film available under the trade designation Kapton from E.I. duPont de Nemours, Wilmington, DE, was used as a thin metal-coated substrate. A chrome layer had previously been deposited onto the Kapton film before the thin layer of copper was deposited. A thick substrate was prepared by electroplating the thin substrate with 150 μin. (4 μm) of copper. The copper surface was cleaned by swabbing with cotton soaked in the etching solution, rinsing with water, and drying.

Donor Sheet

47.17 wt% black pigment available under the trade designation Raven 760 from Columbian Chemicals Co., Tulsa, OK; 47.17 wt% styrene/acrylic resin available under the trade designation Joncryl 690 from Johnson Wax Co., Racine, WI; and 5.66 wt% dispersant available under the trade designation Disperbyk 161 from Byk Chemie was used directly as an 18.8 wt% solids dispersion in Solvent PM (methoxylated propylene glycol) / MEK (3:1). The dispersion was coated onto plain 4 mil PET using a #4 or a #8 Mayer bar (available from R&D Specialties, Webster, NY) and then dried for 2 min at 55°C. A topcoat of Daratak 90L adhesive was applied using a #4 Mayer bar. The donor sheet was dried again for 2 min at 55°C.

Nitric Acid Etching Bath

An acidic etching bath was prepared by diluting concentrated nitric acid with an equal volume of water.

Sulfuric Acid/Peroxide Etching Bath

An acidic etching bath was prepared by diluting 50 ml of concentrated sulfuric acid with 400 ml of water and 50 ml of aqueous hydrogen peroxide.

Example 1

The copper plated Kapton polyimide receptor (thin substrate) was placed in the curved focal plane surface (internal drum) of the laser imager with the copper surface away from the drum. The donor sheet disclosed earlier herein containing Raven black pigment was placed onto the copper surface so that the copper and resist were in contact and the donor was imaged to create circuit and

line patterns. Lines of 30 μm width and 42 μm pitch were demonstrated to be feasible with this method.

The metal surface was patterned by etching the exposed copper with the sulfuric acid/peroxide bath for approximately 3 min at room temperature to completely remove the metal, leaving only the substrate polymer in the areas that did not receive the resist. The resist was removed by wiping with a cotton swab soaked in MEK, but could also be removed by treatment in a basic aqueous solution. The result of the process is a copper circuit on a Kapton polyimide substrate. Photographs of the patterned samples were taken that showed pattern reproducibility and line edge integrity.

Example 2

3M biaxially-oriented 2 mil PET containing slip agent on the opposite side of the vapor coating was sputtered with approximately 5 nm Inconel 600 (alloy of chromium, iron, and nickel) and then vapor coated with approximately 75 nm of copper.

A mixture of 5 g of Daratak 90L adhesive and 45 g of isopropanol/MEK (2:1) was agitated vigorously for 20 min on a shaking table. The resulting translucent adhesive solution was used directly as described below.

An aqueous dispersion (Penn Color, Doylestown, PA, #RD-35088-30, 35% solids) consisting of carbon black, water-soluble acrylic resin available under the trade designation Elvacite 2776 from ICI Acrylics (pigment/binder weight ratio of 1:1), and dimethylethanolamine was coated onto plain 4 mil PET using a #4 Mayer bar and then dried for 3 min at 80°C. A topcoat was applied by coating the adhesive solution using a #3 Mayer bar and drying the sample for 1 min at 80°C.

The copper-coated PET film was placed in the curved focal plane surface (internal drum) of the laser imager with the copper surface away from the drum. The donor sheet was placed onto the copper surface so that the copper and resist were in contact and the donor was imaged to create circuit and line patterns.

The transferred resist pattern on copper-coated PET was the negative of the circuit pattern. An additional 2-10 μm of copper was electroplated onto the

vapor coated seed layer using a standard printed circuit board sulfuric acid bath (Industrial Chemical and Equipment Co., Minneapolis, MN) at approximately 20 A/ft^2. The ink was then stripped by dipping for 30 sec in an aqueous bath containing 1% NaOH and 0.1% Neodol 25-7 non-ionic surfactant composed of a hydrocarbon tail grafted to an ethylene glycol oligomer (available from Shell Oil Co.) at 62°C. The sample was brushed lightly and rinsed with water.

The copper was etched in the areas where the resist pattern was present by dipping it in an aqueous solution containing 10% sulfuric acid and 3% hydrogen peroxide and agitating gently for 30 sec until clear PET was visible. Lines of 25 μm width and 51 μm pitch were demonstrated to be feasible with this method.

Example 3

Acetylene dicarboxylic acid (1.0 g) was added to a solution of 40 g MEK and 9.0 g bis(azidomethyl)oxetane ("BAMO") and heated to 50°C for 10 hours. This material was either used in the MEK solution or it was prepared in an aqueous solvent. A 33.3 g portion of the MEK solution was concentrated on a rotary evaporator to give a viscous semi-solid (less than 3% residual solvent), and redissolved in a mixture of 1.8 g ethanolamine, 44 g isopropyl alcohol, and 88 g water at 40°C.

A dispersion was prepared by mixing (3.22g) bis(azidomethyl)oxetane ("BAMO")/(10g) acetylenedicarboxylic acid ("AD") (prepared as disclosed in the preceding paragraph) 8% solids in 1:2 isopropyl alcohol (IPA)/H_2O with (0.28g) Aquis Carbon Black 47% solids (available from Heucotech LTD 99, Failess Hills, PA.). Six drops of a fluorochemical surfactant, available under the trade designation Fluorad FC 170 from 3M Co., St. Paul, MN, diluted to 5% in 50/50 IPA/H_2O vol % was added to the dispersion. This mixture was coated onto a 2 mil polypropylene film (donor) with a #10 Mayer bar and then air dried.

Daratak 90L adhesive, was diluted to 5.5% solids with a mixture of 2:1 IPA/MEK. It was then coated over the top of the BAMO/AD/carbon black dispersion on the 2 mil polypropylene film with a #10 Mayer bar. This was then dried for five minutes in a 50°C oven.

The receptor was a polyester (PET) film that was vapor coated with a nickel layer and a thin seed layer of copper. A 0.002 inch thick biaxially-oriented PET containing slip agent on the opposite side of the vapor coating was metallized with approximately 5 nm Inconel 600 sputtered on the PET, approximately 75 nm Cu evaporated on the Inconel 600.

The receptor and the donor were placed on a porous ceramic vacuum hold down, facing each other with the donor sheet on top and a vacuum was then applied. A glass mask was placed on top of the donor and then exposed to the output of a short pulse flash lamp system. The linear flash lamps used were constructed of Suprasil quartz tubing with a bore of 0.4 cm and a spacing of 63.5 cm between the electrodes. The lamps were filled with Xenon at a pressure of 200 torr. The flash lamp was mounted in a cusp-shaped reflector coated with a high ultraviolet reflectivity (Acton Research Corporation, coating number 2500). The cusp reflector had a length of approximately 64 cm and a width of 5 cm. The flash lamp system was operated in the simmered mode (2.0 A simmer current). The pulse width of the high energy pulse (FWHM of the current waveform) was 4.5μ sec. A pulse energy of 200 Joules/pulse was used for all samples. The BAMO/carbon black dispersion was blown off the donor sheet onto the unmasked areas of the receptor forming good circuit patterns.

A copper circuit pattern was achieved using two different procedures. The first procedure started with the substrate for the receiving element containing the resist pattern on it. An additional 2-5 μm of copper was electroplated onto the vapor-coated seed using a standard printed circuit board sulfuric acid bath (as supplied by Industrial Chemical and Equipment Co., Minneapolis, MN). 2-5 μm of copper was plated using a plating current density of 20 A/ft^2. The carbon black/adhesive was stripped off using an aqueous 45°C sodium hydroxide solution (1%) containing Neodol 25-7 surfactant. The vapor coated seed layer was removed using a chemical etch composed of 5% sulfuric acid and 5% hydrogen peroxide in distilled water. A 2-5 μm thick copper pattern was left in the electroplated areas. In the second procedure, the receptor with the transferred pattern was placed directly into the sulfuric acid/hydrogen peroxide solution and

the vapor-coated seed layer was removed in the unpatterned areas. The resist was removed using the sodium hydroxide solution, leaving a pattern of thin copper. A thicker layer of imaged copper could be produced by using the desired thickness of copper as the receptor substrate for imaging.

Reasonable variations and modifications are possible from the foregoing disclosure without departing from either the spirit or scope of the present invention as defined in the claims.

WHAT IS CLAIMED IS:

1. A process for preparing printed circuits comprising the steps of:

(a) imagewise exposing a donor element comprising a substrate having coated thereon a resist material comprising a light-to-heat converter dispersed in a binder to a source of electromagnetic radiation under conditions sufficient to transfer said resist material from said donor element to a metal-coated surface of a receiving element;

(b) etching the exposed metal surface of said receiving element; and

(c) removing the resist material from said receiving element.

2. The process according to Claim 1 wherein said resist material is thermally transferred from said donor element to said receiving element.

3. The process according to Claim 1 wherein the source of said electromagnetic radiation is a laser.

4. The process according to Claim 1 wherein said source of electromagnetic radiation is a flash lamp.

5. The process according to Claim 4 wherein said binder of said resist material comprises an acrylic resin.

6. The process according to Claim 4 wherein said binder of said resist material comprises a gas-producing polymer.

7. The process according to Claim 1 wherein said resist material in step (a) further comprises an adhesive topcoat.

8. A process for preparing printed circuits comprising the steps of:

(a) imagewise exposing a donor element comprising a substrate having coated thereon a resist material comprising a light-to-heat converter dispersed in a binder to a source of electromagnetic radiation under conditions sufficient to transfer said resist material from said donor element to a thin metal-coated surface of a receiving element;

(b) metal plating the exposed metal surface of said receiving element;

(c) removing said resist material from said receiving element; and

(d) etching away the areas of the thin metal-coated surface where said resist was present before removal from said receiving element.

9. The process according to Claim 8 wherein said resist material is thermally transferred from said donor element to said receiving element.

10. The process according to Claim 8 wherein said source of electromagnetic radiation is a laser.

11. The process according to Claim 8 wherein said source of electromagnetic radiation is a flash lamp.

12. The process according to Claim 8 wherein said binder of said resist material comprises an acrylic resin.

13. The process according to Claim 8 wherein said binder of said resist material comprises a gas-producing polymer.

14. The process according to Claim 8 wherein said resist material in step (a) further comprises an adhesive topcoat.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/15944

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H05K3/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H05K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 8642 Derwent Publications Ltd., London, GB; AN 86-276504 XP002022152 & JP,A,61 202 890 (DAICEL CHEM IND KK) , 8 September 1986 see abstract	1-3,5,7
Y		6

A	US,A,5 278 023 (BILLS ET AL.) 11 January 1994 cited in the application see abstract	1-3
Y		6

	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
7 January 1997	14. 01. 97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Mes, L

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 8632 Derwent Publications Ltd., London, GB; AN 86-209916 XP002022153 & JP,A,61 144 092 (DAICEL CHEM IND KK) , 1 July 1986 see title ---	1-3
A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 99 (E-0893), 22 February 1990 & JP,A,01 303786 (SHIKOKU CHEM CORP), 7 December 1989, see abstract ---	1,2
A	PATENT ABSTRACTS OF JAPAN vol. 17, no. 103 (M-1374), 2 March 1993 & JP,A,04 292993 (TOPPAN PRINTING CO), 16 October 1992, see abstract -----	1,2,7

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

ational Application No
PCT/US 96/15944

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5278023	11-01-94	EP-A- 0599689	01-06-94
		JP-A- 6239032	30-08-94